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DEPARTMENT OF TRADE
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This is to certify that

the documents annexed hereto are true copies of:

Application forms P.1 and P.3, provisional specification and drawings of South African Patent Application No. 93/6488 as originally filed in the Republic of South Africa on 2nd September, 1993, in the name of TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED, for an invention entitled: "ELECTROCHEMICAL CELL".

aan te
da

RIA

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

24th dag van
day of

February 1994

Registrateur van Patente
Registrar of Patents

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
APPLICATION FOR A PATENT AND
ACKNOWLEDGEMENT OF RECEIPT
(Section 30(1) Regulation 22)

FORM P.1
(to be lodged in duplicate)

REPUBLIC OF SOUTH AFRICA
REVENUE

-2.9.93

R 042.00

THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT
ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE.

IRKOMSTE
REPUBLIEK VAN SUID AFRIKA

A & A SET: 009487 GSK

PATENT APPLICATION NO.	
21	01 936488
71	FULL NAMES(S) OF APPLICANT(S)

TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED

ADDRESS(ES) OF APPLICANT(S)

2nd Floor, Finance Week House, 72 Grayston Drive, Sandton,
Transvaal Province, Republic of South Africa

54 TITLE OF INVENTION

"ELECTROCHEMICAL CELL"

Only the items marked with an "X" in the blocks below are applicable.

<input type="checkbox"/>	The Applicant claims priority as set out on the accompanying Form P.2. The earliest priority claimed is Country: No: Date:
<input type="checkbox"/>	The application is for a patent of addition to patent application no. [21 01
<input type="checkbox"/>	This application is a fresh application in terms of section 37 and based on Application No. [21 01

THIS APPLICATION IS ACCOMPANIED BY:

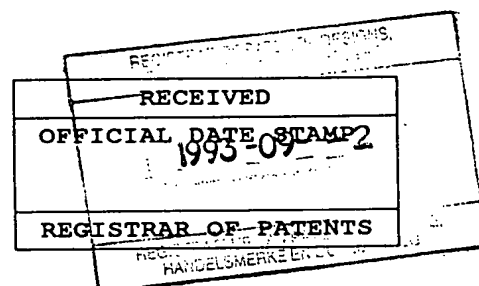
<input checked="" type="checkbox"/>	A single copy of a provisional or two copies of a complete specification of ..10.. pages.
<input checked="" type="checkbox"/>	Drawing of ..3... sheets.
<input type="checkbox"/>	Publication particulars and abstract (Form P.8 in duplicate) (for complete only).
<input type="checkbox"/>	A copy of Figure of the drawings (if any) for the abstract (for complete only).
<input checked="" type="checkbox"/>	An assignment of invention.
<input type="checkbox"/>	Certified priority document(s) (State quantity):
<input type="checkbox"/>	Translation of the priority document(s).
<input type="checkbox"/>	An assignment of priority rights.
<input type="checkbox"/>	A copy of Form P.2 and the specification of RSA Patent Application No. [21 01
<input checked="" type="checkbox"/>	A Form P.2 in duplicate.
<input checked="" type="checkbox"/>	A declaration and power of attorney on Form P.3.
<input type="checkbox"/>	Request for ante-dating on Form P.4.
<input type="checkbox"/>	Request for classification on Form P.9.
<input type="checkbox"/>	Request for delay of acceptance on Form P.4.

74 ADDRESS FOR SERVICE: Adams & Adams, Pretoria

DATED THIS 2ND DAY OF SEPTEMBER 1993

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PATENTS ACT, 1978

DECLARATION AND POWER OF ATTORNEY 2.9.93
(Section 30 - Regulation 8, 22(i)(c) and 33)

REPUBLIC OF SOUTH AFRICA
REVENUE FORM P.3

R 001.00

INKOMSTE
REPUBLIEK VAN SUID AFRIKA
LODGER DAT 570

PATENT APPLICATION NO.		
21	01	936488

A & A REF: V09487 GSK

22 2 SEPTEMBER 1993

FULL NAME(S) OF APPLICANT(S)

71 TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED

FULL NAME(S) OF INVENTOR(S)

72 MICHAEL MAKEPEACE THACKERAY

EARLIEST PRIORITY CLAIMED	COUNTRY	NUMBER	DATE
33	--	31	--

NOTE: The country must be indicated by its International Abbreviation - see schedule 4 of the Regulations

TITLE OF INVENTION

54 "ELECTROCHEMICAL CELL"

I/We Lourence Cornelius Johannes Greyvenstein
hereby declare that :-

1. I/We am/are the applicant(s) mentioned above;

** 2. I/We have been authorized by the applicant(s) to make this declaration and have knowledge of the facts herein stated in the capacity of Chief Executive Officer of the applicant(s);

*** 3. the inventor(s) of the abovementioned invention is/are the person(s) named above and the applicant(s) has/have acquired the right to apply by virtue of the provisions of Section 13 of Act 46 of 1988 and an assignment from CSIR;

4. to the best of my/our knowledge and belief, if a patent is granted on the application, there will be no lawful ground for the revocation of the patent;

**** 5. ~~This is a convention application and the earliest application from which priority is claimed as set out above is the first application in a convention country in respect of the invention claimed in any of the claims; and~~

6. the partners and qualified staff of the firm of ADAMS & ADAMS, patent attorneys, are authorised, jointly and severally, with powers of substitution and revocation, to represent the applicant(s) in this application and to be the address for service of the applicant(s) while the application is pending and after a patent has been granted on the application.

DATED AT JOHANNESBURG, THIS 1st DAY OF SEPTEMBER, 1993


(SIGNATURE(S)
(no legalization necessary)

* In the case of application in the name of a company, partnership or firm, give full names of signatory/signatories, delete paragraph 1, and enter capacity of each signatory in paragraph 2.

** If the applicant is a natural person, delete paragraph 2.

*** If the right to apply is not by virtue of an assignment from the inventor(s), delete an assignment from the inventor(s) and give details of acquisition of right.

**** For non-convention applications, delete paragraph 5.

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FORM P.6

REPUBLIC OF SOUTH AFRICA
Patents Act, 1978

PROVISIONAL SPECIFICATION

(Section 30(1) - Regulation 27)

OFFICIAL APPLICATION NO.

21 01

936488

LODGING DATE

22

2 SEPTEMBER 1993

FULL NAME(S) OF APPLICANT(S)

71

TECHNOLOGY FINANCE CORPORATION (PROPRIETARY) LIMITED

FULL NAME(S) OF INVENTOR(S)

72

MICHAEL MAKEPEACE THACKERAY

TITLE OF INVENTION

54

"ELECTROCHEMICAL CELL"

THIS INVENTION relates to an electrochemical cell. It relates in particular to a rechargeable electrochemical cell.

According to the invention, there is provided a rechargeable electrochemical cell, which comprises

5 as an anode, a lithium metal oxide compound which has a spinel-type framework structure;

as a cathode, a lithium metal oxide compound; and

an electrically insulative lithium containing liquid or polymeric electronically conductive electrolyte between the anode and the cathode, such that, on charging the cell, lithium ions are extracted from the lithium metal oxide compound of the cathode, with the oxidation state of the metal of the cathode thereby increasing, while a concomitant insertion of lithium ions into the spinel-type framework structure of the anode takes place, with the oxidation state of the metal of the anode decreasing correspondingly, and with the reverse reactions taking place during discharge of the cell.

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Spinel compounds have structures that can be represented by the general formula $A[B_2]X_4$ in which the X atoms are arranged in a cubic-close-packed fashion to form a negatively charged anion array comprised of face-sharing and edge-sharing X tetrahedra and octahedra. In the formula $A[B_2]X_4$, the A cations and B cations occupy tetrahedral and octahedral sites respectively. In the ideal spinel structure, with the origin of the unit cell at the centre (3m), the close-packed anions are located at the 32e positions of the space group $Fd3m$. Each unit cell contains 64 tetrahedral interstices situated at three crystallographically non-equivalent positions 8a, 8b and 48f, and 32 octahedral interstices situated at the crystallographically non-equivalent positions 16c and 16d. In the $A[B_2]X_4$ spinel, the A cations reside in the 8a tetrahedral interstices and the B cations in the 16d octahedral interstices. There are thus 56 empty tetrahedral and 16 empty octahedral sites per cubic unit cell.

In the anode of the cell of the present invention, therefore, the B cations of the $[B_2]X_4^{n-}$ host framework structure may be regarded as being located at the 16d octahedral positions, and the X anions as being located at the 32e positions of the spinel structure. The tetrahedra defined by the 8a, 8b and 48f positions and the octahedra defined by the 16c positions of the spinel structure thus form the interstitial space of the $[B_2]X_4^{n-}$ framework structure for the diffusion of mobile Li^+ cations.

The B cations of the framework structure may consist of one cationic type, or more than one cationic type of identical or

mixed valence to provide various $[B_2]X_4^{n-}$ framework structures, the overall charge of which may vary over a wide range.

Spinel compounds having the $[B_2]X_4^{n-}$ framework structure may also be characterized by crystallographic space groups other than the prototypic cubic space group $Fd3m$. For example, in $Li_{1+x}[Mn_2]O_4$ compounds with $0 < x < 1$, ie compounds in which A is Li, and B is Mn, the spinel structure is distorted, as a result of the Jahn-Teller Mn^{3+} octahedral site ions, to tetragonal symmetry, and the compound is characterized by the tetragonal space groups $F4_1/ddm$ or $I4_1/amd$ in which the tetrahedral and octahedral site nomenclature differs from that as defined by the space group $Fd3m$.

Furthermore, the anode need not necessarily be a stoichiometric spinel compound, but can instead be a defect spinel. Defect spinels are well known in the large family of spinel compounds and can have vacancies on the A sites, or on the B sites, or on both the A sites and B sites. For example, compounds can be synthesized in which defects are created by varying the quantity of B cations in the framework structure such that additional Li^+ cations can enter and leave the framework. In these instances additional Li^+ cations can partially occupy the 16d octahedral sites normally occupied by the B-type cations. Under such circumstances these partially occupied octahedra can be considered to form part of the interstitial space. Conversely, compounds can also be synthesized, in which part of the interstitial spaced defined by the 8a, 8b and 38f tetrahedral and

16c octahedral interstices of the spinel structure can be occupied by B-type cations, thereby rendering these particular sites at least partially inaccessible to the mobile Li cations. The $[B_2]X_4^{n-}$ framework structure may in certain instances have to be stabilized by the introduction of a minor proportion of cations other than the mobile Li-type cations or B-type cations within the interstitial space of the framework structure.

In the compound of the anode, B is thus a metal cation. It may be a single metal cation, or a mixture of metal cations.

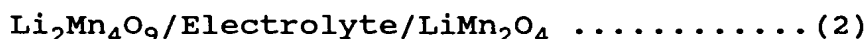
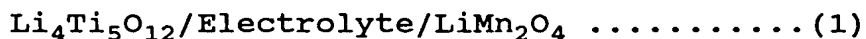
Typically, the compound of the anode may be a stoichiometric spinel such as $Li_4Mn_5O_{12}$, which can be written as $(Li)_{8a}[Li_{0,33}Mn_{1,67}]_{16d}O_4$ in spinel notation; $Li_4Ti_5O_{12}$, which can be written as $(Li)_{8a}[Li_{0,33}Ti_{1,67}]_{16d}O_4$ in spinel notation; or $LiFe_5O_8$, which can be written as $(Li_{0,5}Fe_{0,5})_{8a}[Fe_2]_{16d}O_4$ in spinel notation.

Instead, the compound of the anode may be a defect spinel such as $Li_2Mn_4O_9$, which can be written as $(Li_{0,89}\square_{0,11})_{8a}[Mn_{1,78}\square_{0,22}]_{16d}O_4$ in spinel notation; or $Li_2Ti_3O_7$, which can be written as $(Li_{0,85}\square_{0,15})_{8a}[Ti_{1,71}Li_{0,29}]_{16d}O_4$ in spinel notation. In defect spinels, the distribution of Li^+ on the A and B sites can vary from compound to compound.

The compound of the cathode may also preferably be a stoichiometric or defect spinel compound, with B thereof then also being a single metal cation or a mixture of metal cations.

Typically, the spinel compound of the cathode may be a stoichiometric spinel such as $\text{Li}[\text{Mn}_2]\text{O}_4$ that would typically operate over the range $\text{Li}_x[\text{Mn}_2]\text{O}_4$ where $0,1 \leq x \leq 1,0$; or $\text{Li}_x[\text{Co}_2]\text{O}_4$ where $0,5 \leq x \leq 2,0$. Alternatively, the cathode may have a layered type structure such as those found within the system $\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$ ($0 \leq y \leq 1$) which, in $\text{Li}/\text{electrolyte}/\text{Li}_x\text{Co}_{1-y}\text{Ni}_y\text{O}_2$ cells, typically provide 3,8V to 4,2V versus pure Li over the range $0,4 \leq x \leq 1$.

In general, the anode compound will be selected from those spinel compounds that offer a relatively low voltage vs pure lithium, whereas the cathode compound will be selected from those spinel compounds that offer a relatively high voltage vs pure lithium. For example, a $\text{Li}/\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ cell delivers on discharge at $150\mu\text{A}/\text{cm}^2$ (for $0 < x < 1$) an average voltage of approximately 1,5V, while a $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cell delivers on discharge at $150\mu\text{A}/\text{cm}^2$ (for $0 < x < 1$) an average voltage of approximately 4V. Therefore, a cell in accordance with the invention can have $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ as an anode and $\text{Li}_x\text{Mn}_2\text{O}_4$ as a cathode, and will deliver approximately 2,5V on discharge. In another example, a $\text{Li}/\text{Li}_2\text{Mn}_4\text{O}_9$ cell delivers a voltage of approximately 2,8V over most of the discharge. Thus, a cell in accordance with the invention can have a $\text{Li}_{2+x}\text{Mn}_4\text{O}_9$ anode and $\text{Li}_x\text{Mn}_2\text{O}_4$ as cathode, and delivers approximately 1,2V on discharge, which is the typical voltage of a nickel-cadmium cell. It is convenient to load such cells in a discharged state, ie with the following configurations:



In (1), Li^+ ions are extracted from $\text{Li}[\text{Mn}_2]\text{O}_4$ during charge with a concomitant oxidation of the manganese ions from an average valence of 3,5 to higher values, and inserted into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$

electrode structure with a concomitant reduction of the titanium cations from the average valence state of +4 to lower values. During this process Li^+ ions are shuttled to and fro between the oxide structures without the formation of any metallic lithium, the cell voltage being derived from changes in the oxidation state of the transition metal cations in the anode and cathode structures.

The electrolyte is conveniently a room temperature electrolyte such as LiClO_4 , LiBF_4 , or LiPF_6 dissolved in an organic salt such as propylene carbonate, ethylene carbonate, dimethyl carbonate, dimethoxyethane or appropriate mixtures thereof, or a polymeric electrolyte such as polyethylene oxide (PEO) - LiClO_4 , PEO - LiSO_3CF_3 or PEO - $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ that operates at room temperature or at elevated temperature, for example at about 120°C .

The invention will now be described by way of non-limiting example, and with reference to the drawings in which

FIGURE 1 shows a plot of voltage vs capacity for a known $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell;

FIGURE 2 shows a plot of voltage vs capacity for a known $\text{Li}/\text{LiMn}_2\text{O}_4$ cell;

FIGURE 3 shows a plot of voltage vs capacity for a known $\text{Li}_2\text{Mn}_4\text{O}_9$ cell;

FIGURE 4 shows powder X-ray diffraction patterns of the compounds synthesized in the examples;

FIGURE 5 shows a plot of voltage vs capacity for the cell of Example 1 and which is in accordance with the invention; and

FIGURE 6 shows a plot of voltage vs capacity for the cell of Example 2 and which is in accordance with the invention.

In view thereof that a $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell delivers on discharge at $150\mu\text{A}/\text{cm}^2$ an average voltage of approximately 1.5V, as indicated in Figure 1, and a $\text{Li}/\text{LiMn}_2\text{O}_4$ cell delivers on discharge at $150\mu\text{A}/\text{cm}^2$ an average voltage of approximately 4V, as indicated in Figure 2, a cell in accordance with the invention and having the configuration $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Electrolyte}/\text{LiMn}_2\text{O}_4$ (1) was made up.

EXAMPLE 1

The LiMn_2O_4 spinel compound of the cathode was synthesized by reaction of LiOH and $\gamma\text{-MnO}_2$ (chemically-prepared manganese dioxide, CMD) firstly at 450°C for 48 hours and thereafter at 750°C for 48 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 4a.

A spinel product of approximate composition $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by reaction of Li_2CO_3 and TiO_2 , using a Li:Ti atomic ratio of 1,0:1,1, for 24 hours at 1000°C in air. A slight excess of lithium was used because of the volatility of Li_2O at that temperature. The powder X-ray diffraction pattern of this spinel product is shown in Figure 4c.

A cell of the format $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Electrolyte}/\text{LiMn}_2\text{O}_4$ (1) was then constructed. The electrolyte used was 1M LiClO_4 in propylene carbonate. The first 10 charge/discharge cycles of the cell are shown in Figure 5. A current of 0.1mA was employed for both

charge and discharge. The cell was cycled between upper and lower voltage limits of 2,65V and 1,9V respectively.

In view thereof that a Li/Li₂Mn₄O₉ cell delivers on discharge at 150μA/cm² an average voltage of approximately 2,8V, as indicated in Figure 3, and a Li/LiMn₂O₄ cell delivers on discharge at 150μA/cm² an average voltage of approximately 4V, as indicated in Figure 2, a cell in accordance with the invention and having the configuration Li₂Mn₄O₉/Electrolyte/LiMn₂O₄ (2) was made up.

EXAMPLE 2

The LiMn₂O₄ as synthesized in Example 1, was used also for the cathode of this example.

Li₂Mn₄O₉ was synthesized by reaction of LiOH and MnCO₃ at 345°C for 32 hours. The powder X-ray diffraction pattern of this compound is shown in Figure 4b. The pattern is predominantly characteristic of the Li₂Mn₄O₉ defect spinel phase, but contains in addition a few weak peaks, for example at 42°2θ and 53°2θ, that are indicative of a minor proportion of lithiated γ-MnO₂ phase.

A cell of the following format was constructed:



The electrolyte used was 1M LiClO₄ in propylene carbonate. The first 9 charge/discharge cycles of the cell are shown in Figure 6. A current of 0,1mA was employed for both charge and

discharge. The cell was cycled between upper and lower voltage limits of 0,45V and 1,5V respectively.

These experiments demonstrate the ability of spinel oxides to provide an electrochemical couple for 'rocking chair' rechargeable lithium cells in which lithium ions are transported between two transition metal oxide electrodes having spinel-type structures using a liquid or polymeric electrolyte containing Li^+ ions. The electrochemical cells thus contain no metallic lithium anode, and are therefore inherently safer than lithium cells containing metallic lithium anodes, lithium alloys or indeed even lithium-carbon anodes. In particular, such cells provide an added advantage of providing a more constant operating voltage than lithium carbon anode cells.

Instead of the compounds of the electrodes being oxides, they can be chalcogenides, ie S or Se based compounds, in accordance with the principles of this invention.

DATED THIS 2ND DAY OF SEPTEMBER 1993.


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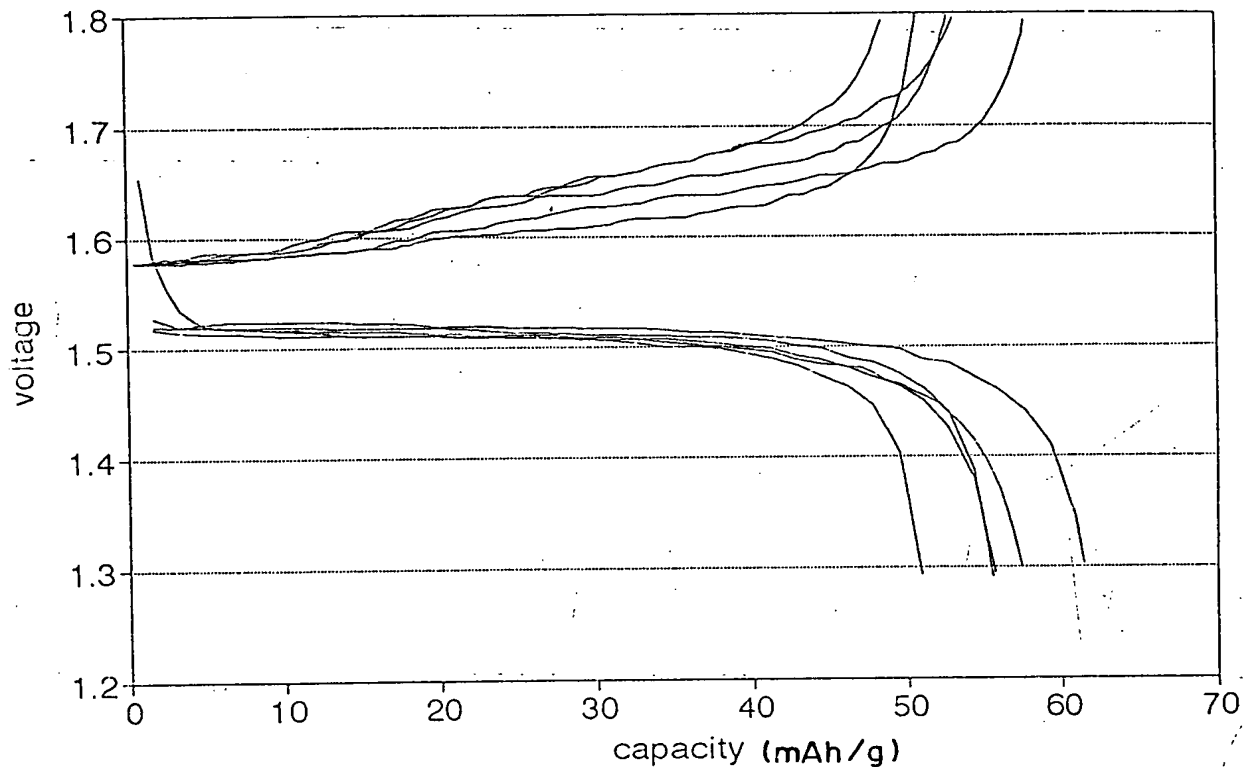


FIG 1

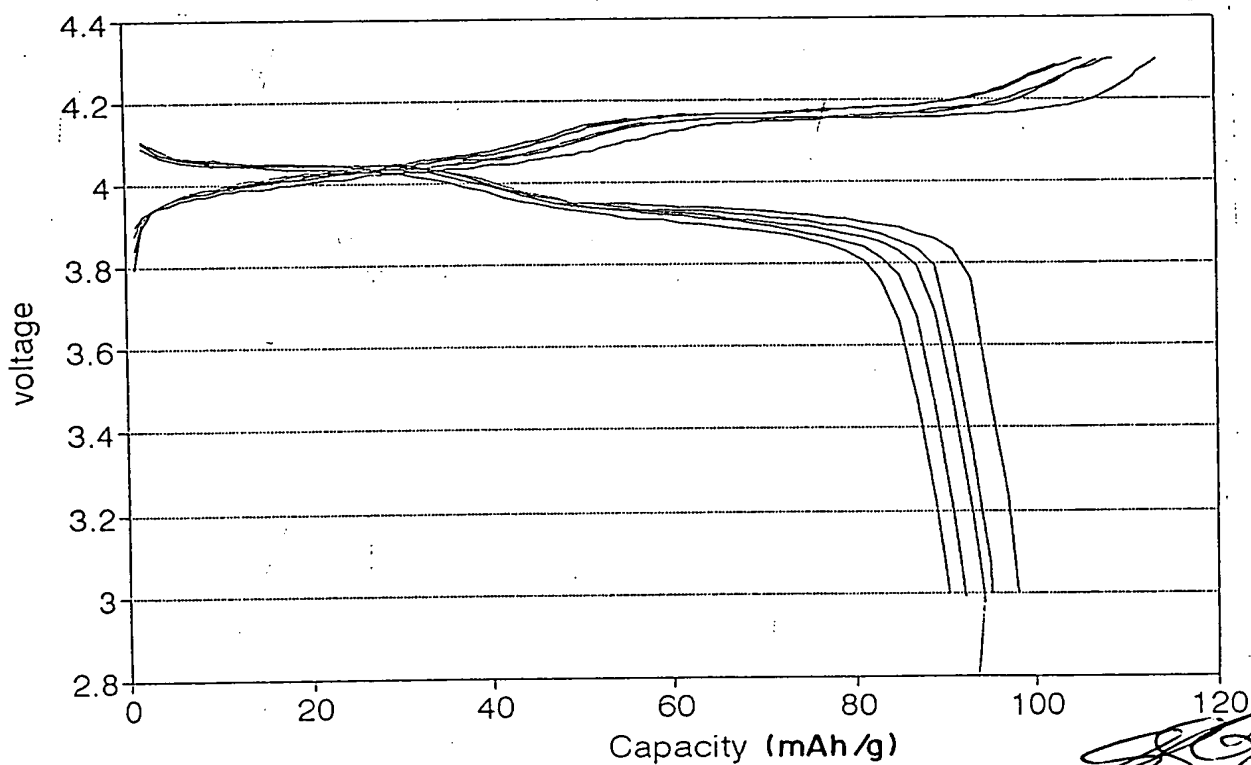


FIG 2

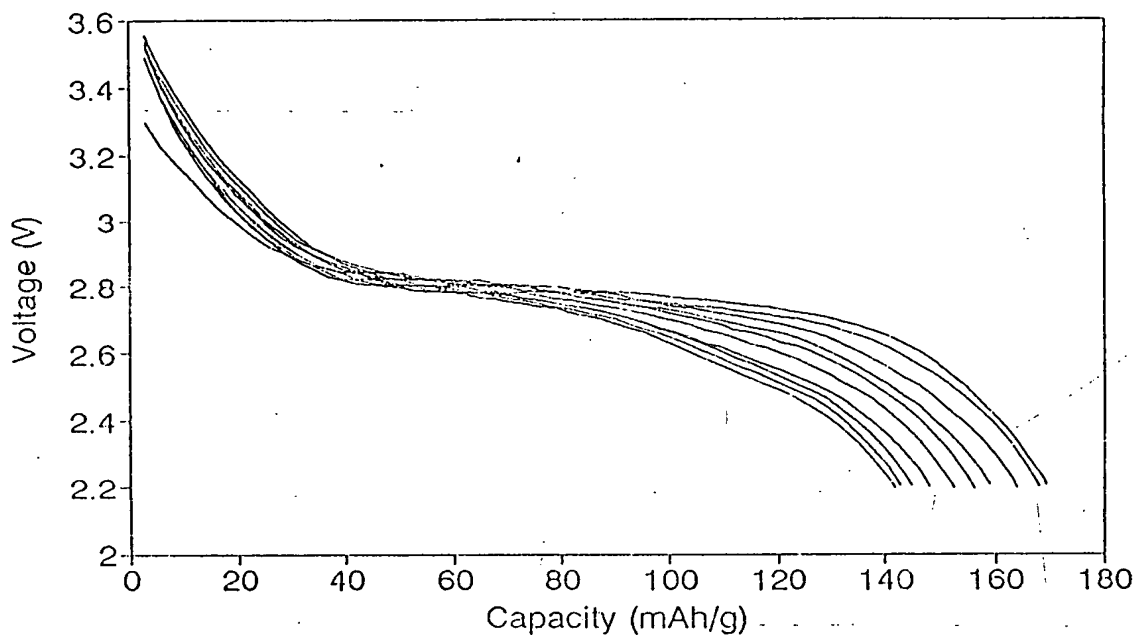
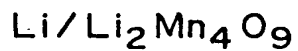


FIG 3

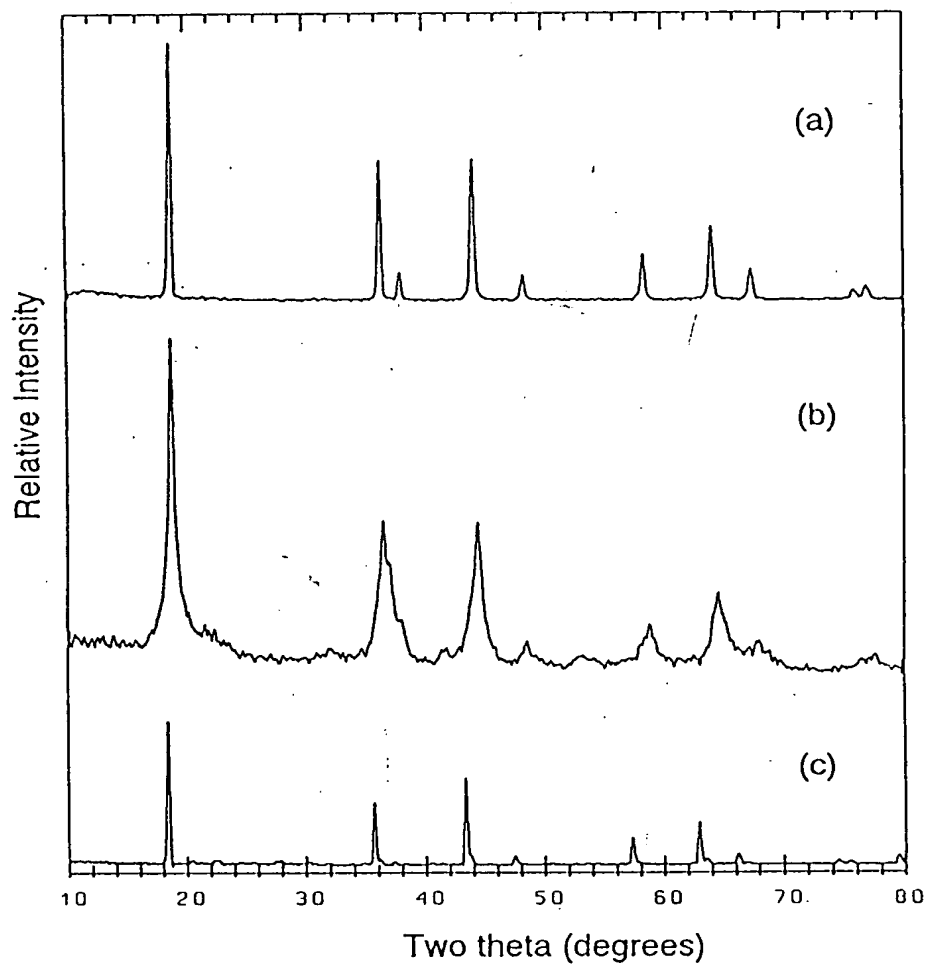


FIG 4

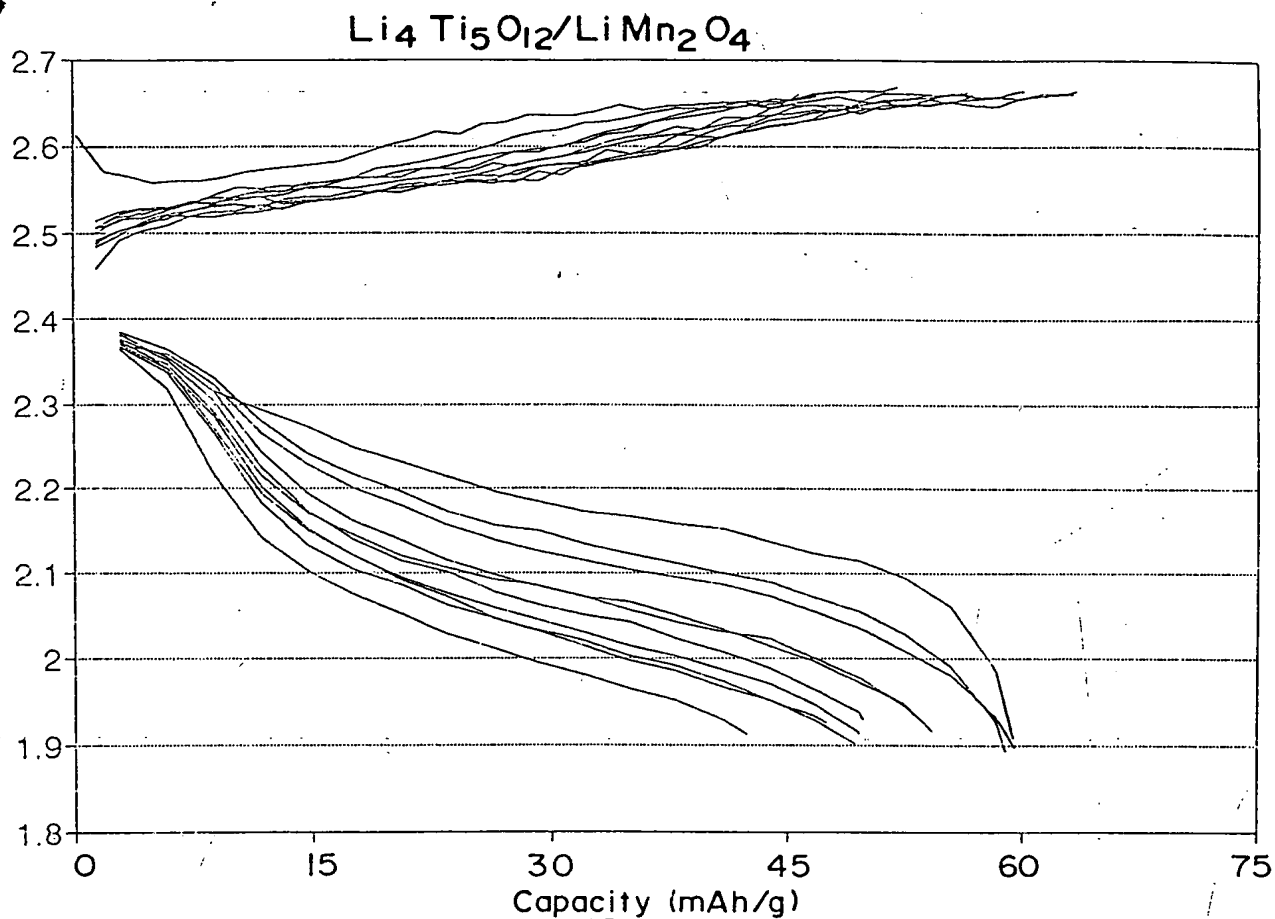


FIG 5

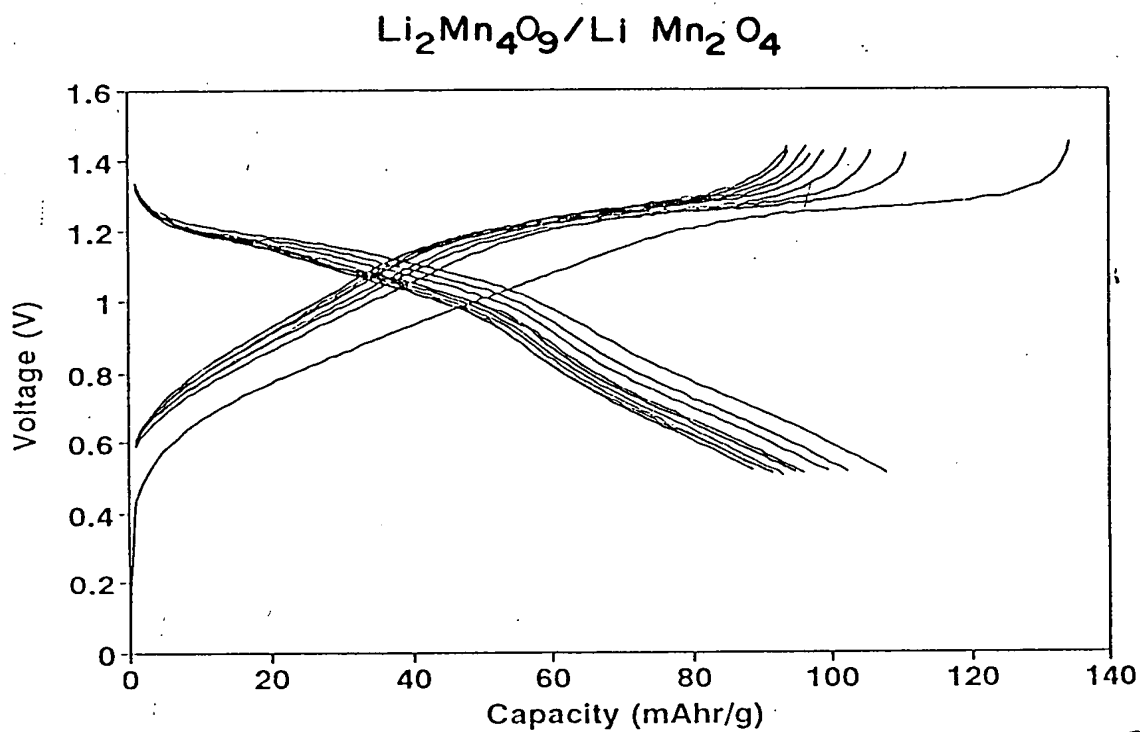


FIG 6